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WASTE INVESTIGATIONS, SEMET-SOLVAY DIVISION, ALLIED CHEMICAL AND DYE CORPORATION, TONAWANDA, NEW YORK. PART I. WASTE SURVEY REPORT. PART II. BIOASSAY INVESTIGATIONS

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Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio

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WASTE INVESTIGATIONS

FOR

INTERNATIONAL JOINT COMMISSION

PART I - WASTE SURVEY REPORT

PART II - BIOASSAY INVESTIGATIONS

HARRIET PLANT

SEMET-SOLVAY DIVISION

ALLIED CHEMICAL AND DYE CORPORATION

TONAWANDA, NEW YORK

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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WASTE INVESTIGATIONS

SEMET-SOLVAY DIVISION

ALLIED CHEMICAL AND DYE CORPORATION

TONAWANDA, NEW YORK

Introduction

During the periods Oct. 28-Nov. 1 and Nov. 7-8, 1956, investigations were conducted to determine the pollutional characteristics of Semet-Solvay oil-gas generator and by-product coke plant wastes which are discharged into the Niagara River.

Part I of this report covers a study of waste flows and certain pollutional characteristics in relation to plant operations.

Part II covers an investigation of the toxicity to fish of some of the plant effluents.

Personnel Participating

Semet-Solvay Division

Mr. H. G. Briggs	Superintendent
Mr. George Meyers	Asst. Superintendent
Mr. Ernest Springer	Chief Chemist
Mr. Robert Shea	Asst. Chief Chemist
Mr. David Zimmer	Chemist
Mr. L. A. Angus	Oil Gas Generator Plant Foreman

Public Health Service

Hayse H. Black	Industrial Wastes Consultant
Croswell Henderson	Aquatic Biologist
H. A. Anderson	Public Health Engineer
M. W. Ruszaj	Chemist

PART I - WASTE SURVEY REPORT

By H. A. Anderson

Purpose

This survey was conducted to determine the current quantities of water polluting materials in process wastes discharged from the Semet-Solvay oil gas generator and by-product coke plants into the Niagara River. No previous data on the wastes from the oil gas generating plant were available as this plant began operation subsequent to the cooperative study conducted in August - November 1948. Data on oil discharges from this plant was particularly desired. This survey is a part of an investigation of Boundary Waters being conducted by the International Joint Commission in conjunction with the New York State Water Pollution Control Board program to achieve the Objectives for Boundary Water Control Adopted by the International Joint Commission.

Organization of the Survey

This survey was cooperatively conducted by the Semet-Solvay Division and the I. J. C. Field Unit of the U. S. Public Health Service. It was initiated by a letter dated May 18, 1956, from the New York State Water Pollution Control Board to the Semet-Solvay Division suggesting that a meeting of company and I. J. C. Field Unit personnel be arranged to discuss the feasibility of a study. A preliminary conference was held on June 7 and at a meeting on October 16, specific arrangements were made for the conduct of the survey.

Duplicate samples were collected and similar analyses of effluents were made by company and I. J. C. chemists. The company provided laboratory space for the use of the I. J. C. Unit personnel and all analytical determinations during the October 28 to November 1 period were carried out in the company

laboratory. The November 7 and 8 analyses were run only by I. J. C. Field Unit personnel in the I. J. C. Field Unit Laboratory.

GENERAL INFORMATION

Location of Plant

This plant is located approximately 1-1/4 mile north of Sheridan Drive on River Road, Town of Tonawanda, New York.

Production Operations

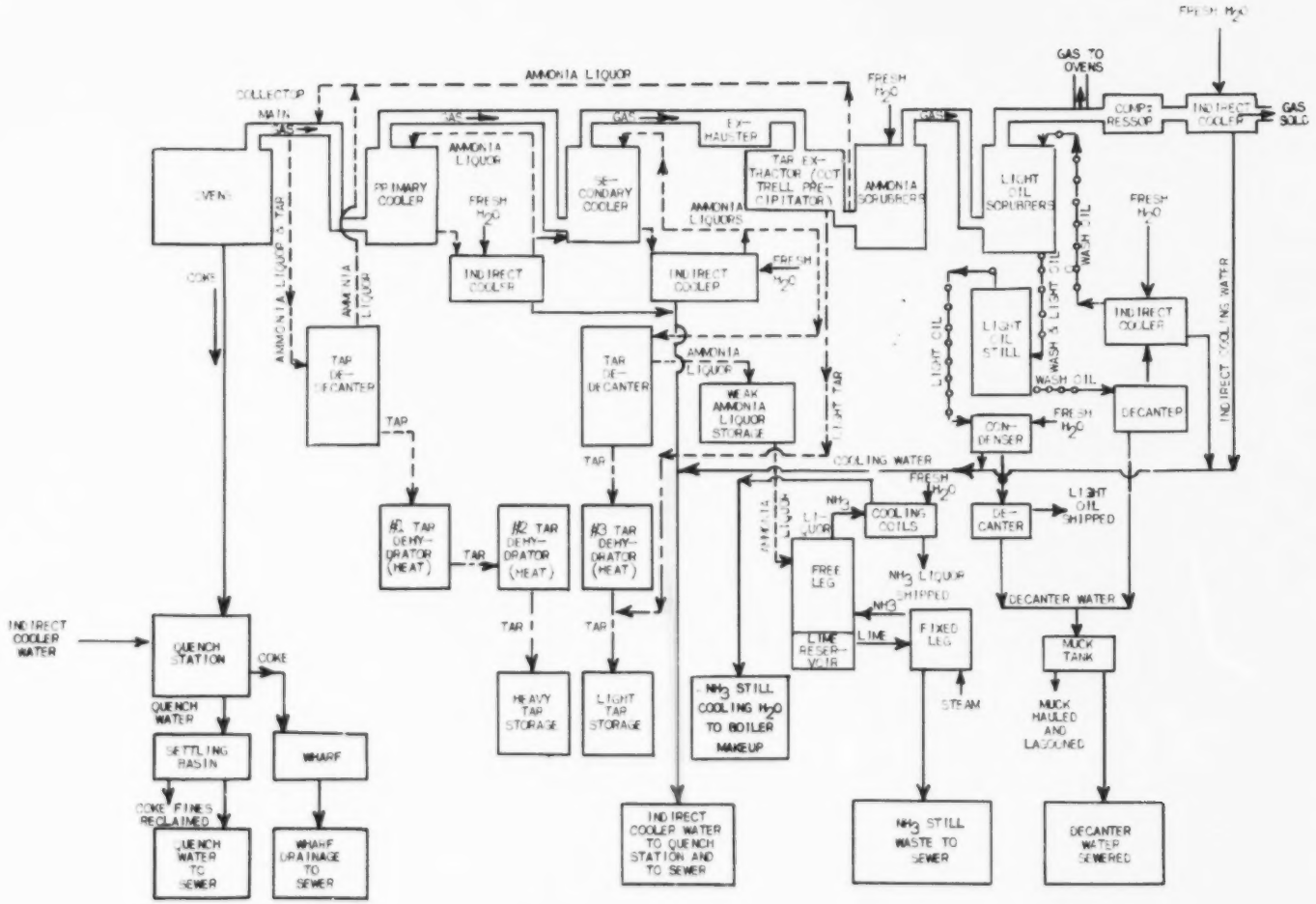
The coke plant produces blast furnace and metallurgical coke and a very limited quantity of domestic coke from coal obtained from Pennsylvania and West Virginia fields. Coking is accomplished in Semet-Solvay design horizontal flue type ovens. By-products include gas, ammonia as 2.4 to 30% NH_3 liquor, tar, pyridine and light oil. The concentrated ammonia liquor is recovered by means of the indirect process. Light oil is not refined and separated into its principal fractions of benzene, toluene and xylene at this plant. A flow chart of the coke plant is shown in Figure 1.

The oil gas generating plant produces an oil gas which is delivered to an adjacent plant for the production of certain petrochemical products. Much of the production and operating features of this plant are classified as trade secrets by the company. Therefore relatively little information on production processes of this plant is available.

Both the coke and oil gas generator plants are operated 24 hours per day and 7 days per week.

Operating Data

A total of 195 ovens are pushed per day. During the periods of this survey daily production was essentially constant at the following rate per 24 hours:



SIMPLIFIED FLOW DIAGRAM

SHOWING LIQUID WASTES DISCHARGED

SEMET SOLVAY DIVISION

ALLIED CHEMICAL AND DYE CORPORATION

Figure 1

Coal charged	2,800 tons (Dry Basis)
Coke produced	2,000 tons (Dry Basis)
Coke oven gas	28.8 million cubic feet
Tar	21,000 gallons
Ammonia as 16-30% NH_3 liquor	60,000 lb. $(NH_4)_2SO_4$ equivalent
Light Oil	7,200 gallons
Pyridine	0
Coking time	15 hours
Coke oven flue temp.	1,300 - 1,360° C. or 2,372 - 2,480° F.

Employees

The total number of employees including office personnel is approximately 400. The maximum number on duty during any 24 hour period does not exceed 265. About 40% of the number are on the day shift with 30% on the other two shifts.

Water Supply

All water is obtained from the Niagara River. The pump station is located adjacent to the river on the south edge of the Wickwire Spencer Steel Division property and upstream from the Steel Plant and Semet-Solvay waste outfalls. Coarse screens prevent debris from reaching the pump intakes. Process water is untreated. Water for drinking and sanitary use is treated by a company water purification plant.

PLANT WASTES

Sewers

All process wastes, septic-tank-treated sanitary wastes from the central locker room and surface run-off from the coke plant drain to a two foot wide rectangular cross section sewer located along the west edge of the plant area. This sewer discharges into a sump at the northwest corner of the property.

Oil gas generator plant wastes drain into a 30 inch diameter sewer which runs in a westerly direction and discharges into the above sump. Untreated sanitary wastes from the office are discharged directly to the sump.

The sump discharges into a sewer extending in a westerly direction which crosses River Road on an overhead bridge. The sewer section crossing the road consists of 24 inch diameter cast iron pipe. It discharges into a sewer on Wickwire Spencer Steel Division property which carries the combined steel plant and Semet-Solvay wastes to the Niagara River.

Coke Plant Wastes

Liquid wastes of this coke plant which are significant from the standpoint of content of polluting materials or volume are:

Quench water. A relatively large volume of water used to cool the incandescent coke. The settling basins for removal of coke fines from the quench water were relatively full of fines at the time of this survey and therefore were not removing the maximum quantity of suspended solids from the sewered quench water.

Cooling Water. A large volume of water used for indirect cooling of recirculating and distilled ammonia liquor, wash oil, light oil compressed gas. This water is normally uncontaminated but may contain significant quantities

of polluting materials in the event of leaks in the coils or tubes.

Ammonia Still Wastes. The liquor resulting from steam stripping ammonia from raw ammoniacal liquor. This waste is normally a principal source of phenols, cyanides and thiocyanates in wastes from this type coke plant.

Light oil and wash oil decanter water. Light oil decanter water is the water decanted from the cooled light oil after separation from the wash oil by direct steam distillation. Wash oil decanter water is the water decanted from the wash oil after the above separation. At this plant the light oil and wash oil decanter water pass through a common muck tank and are discharged to the sewer through a common pipe. → The muck tank provides for further decantation so that any oil which may accumulate may be removed.

Oil Gas Generator Plant Wastes

Tar Separator Effluent: This is an intermittent overflow of excess water from the tar or oil separator. The influent to the tar separator consists of one stream of tar containing water from the oil gas generator and two streams from the two direct type oil gas cooling towers. Detergent is added to this water to reduce the surface tension accomplishing improved separation of the tar. This water is cooled in indirect coolers and recirculated to the oil gas generator and oil gas coolers. With proper operation there appears to be very little build up of water and overflow of wastes from this separator. However, during the first day of the survey there was a significant overflow of oil or tar containing wastes from this separator. Plant officials discovered that this excessive overflow was due to a valve having been left open on a make up water line to the separator. This was corrected before the second day sampling and piping changes to prevent the possibility of a recurrence were in progress before the survey was completed. Any overflow which occurs is discharged into the cooling water collecting

basin of the indirect coolers cooling the recirculating water to the oil gas cooling towers.

Gas Holder Water Seal Overflow. This is an intermittent overflow of oil or tar containing water from the water seal of the oil generator gas holder. Source of this water is condensate from the gas cooling in the holder. It also discharges into the indirect cooling water collecting basin.

Indirect Cooling Water

This water, which has been used for indirect cooling of the water recirculated to the oil gas generator and oil gas cooling towers accounts for almost all the volume of the oil gas generator plant wastes. It is uncontaminated except in the event of breaks in the tubes permitting oil gas cooling tower water to enter it. No leaks were observed during the survey.

SURVEY METHODS

Sample Collection

Uniform portion samples of all effluents studied were collected hourly over an eight hour period beginning at 8:00 AM. Samples for phenol analysis were preserved with $CuSO_4$ and samples for cyanide determinations were preserved by adding sufficient NaOH to provide a pH of 11 or above. For the oil determination a 4 oz. sample was collected hourly and poured into a glass stoppered one liter bottle. In the analysis for oil content both the 4 oz. and liter bottles were rinsed with solvent to recover any oil clinging to the inside of the bottle.

Separate samples were collected for oil determination by Semet-Solvay and U.S.P.H.S. analysts. In the determination of other constituents all analysts used portions of the same samples. The number of effluents sampled was limited by the capacity of the analysts to complete the desired

determinations within 24 hours of sample collection. During the period from 10-28 to 11-1 inclusive samples of intake water, oil gas generator plant effluent, coke plant effluent and combined coke and oil gas generator plant effluent were collected daily. Oil gas holder effluent and tar separator effluent were collected on one day during this period.

On Nov. 7 and 8 samples were collected from the coke quenching station, combined light oil and wash oil decanter, ammonia still #1, ammonia still #2, oil gas holder overflow, oil gas generator plant, coke plant and combined coke and oil gas generator plant effluents for phenol, cyanide and bioassay analyses. Results of bioassay analyses are reported in Part II.

Analytical Methods

Analysis for cyanide, oil, phenol and pH were made by methods adopted as official methods for Boundary Water quality by the Board of Technical Advisors to the International Joint Commission. Acidity, alkalinity, and solids determination were made by procedures according to those given in "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" published by the American Public Health Association.

Flow Measurements

The discharge volumes of coke plant wastes, oil gas generator plant wastes and combined oil gas generator and coke plant wastes were measured by a Price current meter. Measurement of the coke plant wastes were made in the rectangular cross section sewer at a point approximately 15 feet upstream from the point of discharge into the sump. A Friez water stage recorder was installed on this sewer during several days of the survey. The charts obtained indicated essentially constant and equivalent flows during all 24 hour periods checked. It is believed that the flow measurements of this waste are accurate within the limits of five per cent.

Oil gas generator plant waste flow was measured in a manhole approximately 125 feet upstream from the outfall discharging into the sump. The Friez water level recorder indicated that flows fluctuated somewhat over short intervals of time (approximately 10 minutes), but hourly averages were uniform over 24 hour periods of time. Because of this fluctuation, the measurements are somewhat less accurate than those of the coke plant sewer.

The volume of the combined plant effluents was measured in a tee in the 24 inch cast iron sewer pipe at a point on Wickwire Spencer Division property just upstream from where the pipe goes underground. The high flow velocity in this sewer resulted in considerable turbulence when the current meter was introduced. Current meter determination under these conditions may be expected to be somewhat lower than the actual flow.

The combined light oil and wash oil decanter wastes were measured by timing the discharge of a known quantity with a stop watch. The volume of ammonia still wastes was calculated from the measured feed volume and steam introduced.

RESULTS

Flow Measurements

Effluent	Date	Type of Meas.	Flow
Oil Gas Generator Plant	10-18-56	Large Price Current Meter	2.737* #
Oil Gas Generator Plant	10-31-56	" " " "	2.19
" " " "	11-1-56 11:00 AM	" " " "	1.483
" " " "	11-1-56 3:45 PM	Small " " "	1.62
" " " "	11-1-56	Large " " "	1.52
Average			1.73
Coke Plant Sewer	10-18-56	Large Price Current Meter	11.5*
" " "	10-30-56	" " " "	11.4
" " "	11-1-56	" " " "	11.1
Average			11.25
Combined Coke and Oil Gas Generator Plants (sum of individual measurements)			13.0
Combined Coke and Oil Gas Plant Effluent	10-30-56	Large Price Current Meter	12.1
" " "	10-31-56	" " " "	12.05
Average			12.1
No.1 Ammonia Still	11-7-56	Calculated from input	0.153
No.1 Ammonia Still	11-8-56	" " "	0.137
Average			0.145
No.2 Ammonia Still	11-7-56	Calculated from input	0.140
No.2 Ammonia Still	11-8-56	" " "	0.117
Average			0.129
Combined Light and Wash Oil Decanter	11-7-56 11-8-56	Timed a Measured Volume	0.037
" " "	11:30 AM 11-8-56	" " " "	0.042
" " "	3:45 PM	" " " "	0.036
Average			0.038

* Trial run measurements made before the survey and not included in the averages.

† During this period there was an above-normal discharge from the tar separator due to addition of excess make-up water.

The averages of the flow measurements of each effluent were used in the calculations in this report. The combined coke and oil gas plant flow used in the calculations is the one obtained by summing the measured individual plant waste flows. Conditions for measuring the combined effluent were such that the value obtained was expected to be somewhat low. It should be noted that the variation between the sum of the individual effluent measurements and the combined effluent was less than 10%.

ANALYTICAL RESULTS

The results of the waste determinations are presented in Tables 1 through 5.

The analytical results reported are those of the I.J.C. Field Unit laboratories. The chemical determinations of the two laboratories were in substantial agreement. The reported net concentration of materials in the waste is the concentration found in the wastes less the concentration found in the intake water. The net value is assumed to be the quantity contributed by the plant. The quantity present in the intake water was significant only in the case of oil and solids determinations.

Oil and Ether Extractable Material

The oil content of the oil gas generator plant varied from 3.0 to 8.0 ppm on the three days of sampling with normal operations. The effect of

adding excess make-up water to the tar separator on October 28 is indicated by the 18 ppm of oil in the effluent on that date. This is more than twice the amount of oil discharged to waste on the other days sampled.

The concentration of oil in the coke plant effluent varied from 2 to 8 ppm and in the combined plant effluent varied from 2 to 12 ppm. The value of 12 ppm in the combined effluent on October 31 is higher than the concentration in either of the separate plant effluents. Semet-Solvay analysts found 5 ppm in their sample. It appears that the sample analysed by the I. J. C. chemist may not have been representative.

Comparison of the results of this survey with the 1948 survey indicates relatively little change in the total quantity of oil discharged to waste.

Phenols

Of particular interest is the gradual daily increase of phenols in both the coke plant and combined plant effluents from the first day (10-28) to the last day (11-1) of the five day survey. During this period, routine plant control analyses of the Semet-Solvay laboratory showed that the concentration of phenols in the weak ammonia liquor feed to the still was lower than usual and also increased towards the end of the survey.

As part of the bioassay study, phenols were also run on these effluents on 11-7 and 11-8. They were significantly higher, indicating that the increase continued during the interim between the samplings.

Plant officials reported that their routine analyses have shown marked gradual increases or decreases of phenol concentration in the ammonia liquor feed to the still. Coking temperature and other operations known to affect phenol concentrations in ammonia liquor feed as well as in the waste do not

vary sufficiently to explain the change in quantity of phenols. It is believed that the results obtained in this survey indicate that the phenols discharged vary significantly. The plant chemists are concerned with this phenomena and are attempting to find the reason for it. The average daily quantity of phenols found in the coke plant wastes during the period 10-28 to 11-1-56 (1410 lbs.) was significantly lower than the 2009 lbs. found during the 1948 survey. The 2170 lbs. of phenols found on 11-7 and 11-8, 1956 is somewhat higher.

Phenols in the oil gas generator plant effluent ranged from 5.8 to 28.9 pounds per day which is considerably less than the coke plant discharge.

Suspended Solids

It was possible to make suspended solids determinations on only one day of this survey. Too much confidence can not be placed on a single analysis but it is interesting to note that the quantity of suspended solids found in the wastes in 1956 is markedly lower than during the 1948 study. There is no known reason to expect such a reiuction.

Cyanide

Cyanide determinations of less than 0.01 ppm are reported as 0 in this report. The maximum concentration of cyanide found in the coke plant effluent during the 10-28 to 11-1 period was 0.02 ppm as compared to 2.6 ppm maximum concentration found during the 1948 survey and 1.5 ppm found on November 8.

The quantity of cyanide in the ammonia still wastes and light oil decanter water was significantly higher on 11-8 than on 11-7, the only two days this determination was made. The quantity in the total coke plant

wastes was also significantly higher on 11-8 which tends to substantiate that the increase actually occurred and the variation found was not due to error in sampling or analysis of an individual sample. The reason for the marked increase is not known.

Alkalinity, Acidity, and pH

The change in alkalinity, acidity, and pH of the effluents as compared to the intake water is not extreme.

TABLE 1

ANALYSIS OF OIL AND PHENOL CONTENT
OF INTAKE WATER AND EFFLUENTS

Source	Date 1956	Flow mgd	OIL Gross ppm	OIL Gross lb/day	OIL Net ppm	OIL Net lb/day	PHENOL Gross ppm	PHENOL Net ppm	PHENOL Net Discharge lb/day
Intake Niagara River	10/28		3				.018		
	10/29		2				.059		
	10/30		-				.000		
	10/31		1				.043		
	11/1		1				.000		
AVERAGE			1.8				.024		
Tar Separator Effluent	10/28		428.0		425.0		8.3	8.3	
Oil Gas Holder Overflow	11/1		86.0		85		17.6	17.6	
	11/7				139			25.4	
	11/8							24.5	
AVERAGE	11/7&8				139			24.9	
Oil Gas Generator Plant Effluent	10/28	1.73	18*	260*	15*	216 *	1.4*	1.4	20.2
	10/29	1.73	7	101	5	72	1.5	1.5	21.6
	10/30	1.73	-	-	-	-	1.0	1.0	14.4
	10/31	1.73	8	115	7	101	0.4	0.4	5.8
	11/1	1.73	3	43	2	29	1.6	1.6	23.1
AVERAGE		1.73	6	86.3	4.7	67	1.18	1.2	16.8
	11/7	1.73						2.0	28.9
	11/8	1.73						2.0	28.9
AVERAGE,	11/7&8	1.73						2.0	28.9
Quench Water	11/7						1.5	1.5	
Light and Wash Oil Decanter Water	11/7	0.038						11.5	3.64
	11/8	0.038						8.8	2.79
AVERAGE,	11/7&8							10.1	3.21
Ammonia Still #1	11/7	0.153						742	947
	11/8	0.137						845	964
AVERAGE,	11/7&8	0.145						793	955

TABLE 1 (Cont'd)

ANALYSIS OF OIL AND PHENOL CONTENT
OF INTAKE WATER AND EFFLUENTS

Source	Date 1956	Flow mgd	OIL Gross ppm	OIL Gross lb/day	OIL Net ppm	OIL Net lb/day	PHENOL Gross ppm	PHENOL Net ppm	PHENOL Net Discharge lb/day
Ammonia Still #2	11/7	0.140						900	1050
	11/8	0.117						791	770
AVERAGE, 11/7&8		0.128						845	910
Total Ammonia Still AVERAGE		0.273						845	1865
Coke Plant Effluent	10/28	11.25	5	469	2	188	13.0	13.0	1220
	10/29	11.25	6	563	4	376	13.4	13.4	1257
	10/30	11.25	8	750	6	563	14.9	14.9	1399
	10/31	11.25	3	281	2	188	16.7	16.7	1568
	11/1	11.25	2	188	1	94	17.1	17.1	1604
AVERAGE		11.25	4.8	451	3	282	15.0	15.0	1410
	11/7	11.25					23.6	23.6	2210
	11/8	11.25					22.7	22.7	2130
AVERAGE, 11/7&8		11.25					23.1	23.1	2170
Combined Oil, Gas, Generator and Coke Plant	10/28	13.0	11*	1193*	8*	867*	11.6	11.6	1258
	10/29	13.0	4	433	2	216	11.6	11.6	1258
	10/30	13.0	-	-	-	-	12.8	12.8	1389
	10/31	13.0	12	1300	11	1193	13.9	13.9	1508
	11/1	13.0	2	216	1	108	14.9	14.9	1618
AVERAGE		13.0	6	650	4.7	508	13.0	13.0	1406
	11/8	13.0					20.0	20.0	2160

* Not included in the averages.

SEMET-SOLVAY

TABLE 2
ACIDITY, ALKALINITY, CYANIDE AND pH
ANALYSES OF INTAKE WATER AND EFFLUENTS

Source	Date 1956	Flow mgd	Cyanide ppm	Cyanide lb.per day	Alkalinity ppm	Acidity ppm	pH
Intake	10/28		0		-	-	7.1
Niagara	10/29		0		84	1	-
River	10/30		-		-	-	-
	10/31		-		-	-	7.3
	11/1		-		-	-	7.7
AVERAGE			0		84	1	7.3
Tar	10/28		0				7.1
Separator	11/1						7.7
Effluent							
AVERAGE			0				7.4
Oil Gas	11/1		0				
Holder	11/7		0				
Overflow	11/8		1.30				
Oil Gas	10/28	1.73	0	0	-	10	7.3
Generator	10/29	1.73	0	0	84	-	7.4
Plant	10/30	1.73	0	0	-	-	-
Effluent	10/31	1.73	0	0	-	-	7.2
	11/1	1.73	0	0	-	-	7.3
AVERAGE		1.73	0	0	84	10	7.3
	11/7	1.73	0.03	0.390	-	-	-
	11/8	1.73	0.0	0.0	-	-	-
AVERAGE		1.73	0.02	0.20	-	-	-
Quench	11/7		0.38				
Water							
Light and	11/7	.038	3.88	1.2			
Wash Oil	11/8	.038	116.0	36.8			
Decanter							
Water							
AVERAGE		.038	59.94	19.0			
Ammonia	11/7	0.153	2.60	3.3			
Still #1	11/8	0.137	41.0	46.7			
AVERAGE		0.145	21.8	25.0			

TABLE 2 (Cont'd)
ACIDITY, ALKALINITY, CYANIDE AND pH
ANALYSES OF INTAKE WATER AND EFFLUENTS

Source	Date 1956	Flow mgd	Cyanide		Alkalinity	Acidity	pH
			ppm	lb.per day	ppm	ppm	
Ammonia	11/7	0.140	2.40	2.8			
Still #2	11/8	0.117	5.00	4.9			
AVERAGE		0.128	3.70	3.8			
Total Ammonia Still							
AVERAGE		0.273		28.8			
Coke Plant	10/28	11.25	0.01	0.9	-	-	7.4
Effluent	10/29	11.25	0.0	0.0	86	12	7.1
	10/30	11.25	0.0	0.0	-	-	-
	10/31	11.25	0.02	1.9	-	-	7.1
	11/1	11.25	0.01	0.9	-	-	7.8
AVERAGE		11.25	0.01	0.7	-	-	7.3
	11/7	11.25	0.23	21.0	-	-	-
	11/8	11.25	1.50	141.0	-	-	-
AVERAGE		11.25	0.86	81.0	-	-	-
Combined	10/28	13.0	-	-	-	-	-
Oil Gas and	10/29	13.0	0	0	88	10	7.5
Coke Plant	10/30	13.0	-	-	-	-	-
Effluent	10/31	13.0	-	-	-	-	6.8
	11/1	13.0	-	-	-	-	7.7
AVERAGE		13.0	0	0	88	10	7.3
	11/8	13.0	1.40	157.0	-	-	-

TABLE 3

ANALYSIS OF SOLIDS CONTENT OF INTAKE WATER AND EFFLUENTS

Source	Date 1956	Flow mgd	SUSPENDED SOLIDS Conc. in ppm Gross	SUSPENDED SOLIDS Conc. in ppm Net	SUSPENDED SOLIDS Disch. lbs/day Gross	SUSPENDED SOLIDS Disch. lbs/day Net	TOTAL SOLIDS Conc. in ppm Gross	TOTAL SOLIDS Conc. in ppm Net	TOTAL SOLIDS Disch. lbs/day Gross	TOTAL SOLIDS Disch. lbs/day Net
Intake Niagara River	10/29		10				246			
Oil Gas Generator Effluent	10/29	1.73	31	21	447	303	352	106	5080	1530
Coke Plant Effluent	10/29	11.25	44	34	4130	3190	520	274	48800	25700
Combined Oil Gas and Coke Plant Effluents	10/29	13.0	36	26	3900	2820	492	246	53200	26700

TABLE 4

SUMMARY OF NET QUANTITY OF CONSTITUENTS IN WASTES

Source	Period	OIL		PHENOL		CYANIDE		SUSPENDED SOLIDS		TOTAL SOLIDS	
		Lbs.per 24 Hrs.	Lbs.per 1000 tons dry coal	Lbs.per 24 Hrs.	Lbs.per 1000 tons dry coal	Lbs.per 24 Hrs.	Lbs.per 1000 tons dry coal	Lbs.per 24 Hrs.	Lbs.per 1000 tons dry coal	Lbs.per 24 Hrs.	Lbs.per 1000 tons dry coal
Light and Wash Oil Decanter Water	Nov.7-8			3.21	1.1	18.5	6.6				
Ammonia Still No.1	Nov.7-8			955	341	25.0	8.9				
Ammonia Still No.2	Nov.7-8			910	325	3.9	1.4				
Total Ammonia Still	Nov.7-8			1865	667	28.9	10.3				
Coke Plant Effluent	10/28to11/1	282	101	1410	504	7.5	2.7	3190	1140	25,700	9190
	Nov.7-8			2170	775	81.0	28.9				
Oil Gas Plant Effluent	10/28to11/1	67		16.8	6.0	0.0	0.0	303		1,530	
	Nov.7-8			28.9	10.3	0.2	0.1				
Total Waste	10/28to11/1	508	181	1406	522			2820	1010	26,700	9550
	Nov.7-8			2160	771	151.0	54.0				

TABLE 5

COMPARISON OF GROSS WASTE LOAD IN POUNDS PER DAY WITH 1948 SURVEY

Source	OIL		PHENOL			CYANIDE			SUSPENDED SOLIDS		TOTAL SOLIDS	
	Nov. Dec. 1948	10/28-11/1 1956	Nov. Dec. 1948	10/28-11/1 1956	11/7-8 1956	Nov. Dec. 1948	10/28-11/1 1956	11/7-8 1956	Nov. Dec. 1948	10/28-11/1 1956	Nov. Dec. 1948	10/28-11/1 1956
Ammonia Still Waste			1,956	-	1,865	61.3	-	28.8	-	-	-	-
Coke Plant Effluent	578	451	2,009	1,410	2,170	120.2	7.5	81.0	9,920	4,130	45,800	48,700
Oil Gas Generator Plant	-	86.3	-	16.7	28.9	-	0	0.20	-	447	-	508
Total Waste Discharged	578	650	2,009	1,406	2,160	120.2	0	-	9,920	3,900	45,800	53,400

PART II - BIO-ASSAY INVESTIGATIONS

By Croswell Henderson

Purpose

This section of the report covers an investigation of the toxicity to fish of certain process and final effluents of the Semet-Solvay Division by-product coke and oil gas generator plants.

By-product coke plant wastes contain some chemical compounds which are known to be toxic to aquatic life in low concentrations. Some of these chemicals, when mixed with, or under the influence of other non-toxic components of the effluent or receiving water, may exert an entirely different toxicity from that of pure compounds. Bio-assays were made to evaluate directly the toxicity of these chemically complex wastes.

Organization of Study

Bio-assays were made on samples of effluents collected on November 7 and 8, 1956. Semet-Solvay and Public Health Service personnel collaborated in collecting 8-hour composite samples. The Public Health Service performed bio-assays in laboratory space provided by the National Aniline Division - Allied Chemical and Dye Corporation in Buffalo. Plant operations, effluent flows, and other information pertinent to the bio-assay studies are contained in Part I of this report.

Bio-Assay Methods

Bio-assays were made essentially by the method recommended by the Toxicity Subcommittee of the Federation of Sewage and Industrial Wastes Associations (Sewage and Industrial Wastes, Vol.23, No.11, 1380, Nov.1951). This method consists of preparing various concentrations of effluent in a

selected dilution water, adding the test fish and observing their reactions over a definite time period. For ease in the plotting and interpreting of results it is desirable to make up test solutions with the percentage of effluent in a logarithmic series as 10, 5.6, 3.2, 1.8, 1.0, etc.

As the effluents were of unknown toxicity, exploratory or small scale tests were made to determine the approximate toxic range. Test solutions were prepared over a wide range of concentration (e.g., 100, 10, and 1.0 per cent effluent). Two fish were added to 2 liters of each concentration in 6-1/2 inch diameter, 1 gallon widemouth glass bottles. Observation for relatively short time periods indicated test concentrations necessary for the full scale experiments.

In full scale bio-assays, 10 fish are normally used for each test concentration. Five fish are added to 10 liter duplicate samples in 5 gallon widemouth glass bottles, 10 inches in diameter. In these tests, however, duplicates were not used. The bio-assay results are based on single samples containing 5 fish in 10 liters. The intermediate concentrations tested were dependent upon information obtained from the exploratory tests. For example, if fish were killed in concentrations above 10 per cent and not affected in concentrations of 1 per cent, intermediates were set up within this range (e.g. 10, 5.6, 3.2, 1.8, and 1.0 per cent concentration of effluent).

The dilution water used was raw Lake Erie water obtained at the Buffalo, New York, water plant. This water was hauled into the laboratory, allowed to come to room temperature, and aerated vigorously for at least one hour to bring it to equilibrium with atmospheric gases. Characteristics of this water at time of use were as follows: Dissolved oxygen 7.6-8.2 ppm; pH 8.0-8.2; total alkalinity ($CaCO_3$) 94-100 ppm; total acidity ($CaCO_3$) 0-1 ppm; versenate hardness ($CaCO_3$) 120-135 ppm.

The test fish used were fathead minnows (Pimephales promelas), ranging in length from 2 to 2-1/2 inches and in weight from 1 to 1-1/2 grams. These fish were obtained in uniform lots from the Newtown, Ohio, Fish Hatchery and acclimated to laboratory conditions. This species is of intermediate tolerance to chemicals comparable to bass, sunfish, perch, and other warm water species, and will tolerate fairly low oxygen conditions (1-2 p.p.m.).

The bio-assays were made at ordinary laboratory temperatures which were within the range from 22° to 25° C. and compare favorably with maximum summer water temperatures in this area.

The tests are designed so that generally no oxygenation or aeration is needed. Absorption of atmospheric oxygen by the exposed water surface is normally adequate for fish requirements during the test period. However, in some of the bio-assays, high oxygen demand effluents caused oxygen depletion. When necessary, dissolved oxygen was maintained by bubbling pure oxygen through the test solution by means of a suitable arrangement of valves and small tubing. The rate (60-180 bubbles per minute) was adjusted to maintain adequate oxygen for fish survival with minimum agitation in order to prevent the loss of volatile materials.

Physical and chemical determinations (temperature, dissolved oxygen, pH, alkalinity, and hardness) were made on each concentration initially, after fish mortality, or at the completion of the test. This was done primarily to detect low D.O. levels so they could be controlled and to differentiate between fish mortality due to oxygen deficiency or acidity and toxic properties.

Effluents were normally brought into the laboratory in the afternoon immediately following collection and exploratory tests were set up at once.

Observations made the following morning furnished information on the toxicity of the wastes essential for settling up the full scale tests.

Fish reactions were observed over a 96 hour period. From the mortality in different concentrations, 24, 48, and 96 hour TL_m (Median tolerance limit) values were obtained. The median tolerance limit is the concentration of effluent in dilution water that kills just 50 per cent of the test fish. These values were obtained by straight line graphical interpolation from points representing per cent survival of fish and log concentrations of effluents which bracketed the 50 per cent point.

The 96 hour TL_m was used to compute the dilution ratio, which is the ratio of a unit volume of effluent to dilution water which produces a 50 per cent mortality of the test fish. This ratio times the effluent flow gives the dilution volume or the total flow or volume of receiving water required to reduce the toxicity of the effluent to where a 50 per cent mortality of the test fish is produced. The following formula may be used for directly computing this dilution volume:

$$\frac{100 - TL_m}{TL_m} \times \text{Effluent Flow} = \text{Dilution Volume}$$

The dilution volumes represent conditions which would cause direct injury to fish upon short time exposure and are a direct comparative measure of toxicity. Liberal application factors must be applied to these results for complete protection of aquatic life. These factors are based on the following major considerations:

(1) The bio-assay procedure measures 50 per cent mortality during a relatively short time period in non-renewed solutions. This must be related to

concentrations having no effect during continuous long time exposure.

(2) Test data apply directly to the species of fish used. While fathead minnows are of intermediate tolerance and compare favorably with many warm water "game" fishes, some locally important species of fish and fish food organisms may be more sensitive. Bio-assays conducted on other coke plant wastes with a locally important forage fish, the emerald shiner (Notropis atherinoides), indicated this species was approximately twice as sensitive as fathead minnows.

(3) Some effluents may vary in toxicity. A few samples may give an indication of toxicity but maximum conditions may be missed. In many situations, maximum conditions of toxicity are the limiting factor as far as aquatic life is concerned.

(4) Some conditions which may generally reduce but in some cases increase the magnitude of the application factor are the loss of volatiles, hydrolysis, oxidation, precipitation, and changes in water quality characteristics of the receiving water.

Based on the best available information, as much as 10 times the computed dilution volume may be necessary for protection of aquatic life in the receiving water.

RESULTS

Physical and Chemical Characteristics

A general description and some of the physical characteristics of the effluent samples collected for the bio-assay studies are shown in Table 6.

Dissolved oxygen values were quite low in all samples except the coke plant effluent, coke quench water, and indirect cooling water. Values for

TABLE 6 - PHYSICAL AND CHEMICAL DATA

SEMET-SOLVAY EFFLUENTS

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppm	Cyanide ppm
Combined Sewer (Oil Gas Generator and Coke Plants	11-7	Grayish tan Oil and medicinal Slightly turbid	0.2	7.8	80	4	195	-	-
"	11-8	"	1.4	7.7	94	8	150	20.0	1.4
Niagara River Intake	11-7	Colorless No odor Clear	4.4	7.6	90	4	145	-	-
Oil gas generator plant	11-7	Grayish-tan Strong medicinal and coal gas Slightly turbid	0.0	7.2	82	12	150	2.0	.03
"	11-8	"	0.2	7.4	88	10	150	2.0	0
Oil gasholder overflow	11-7	Rusty brown Coal gas odor Very turbid	0.0	6.5	120	124	70	25.4	0
"	11-8	"	-	-	-	-	-	24.5	1.3
Coke Plant	11-7	Grayish tan Strong medicinal Slightly turbid	4.8	8.2	92	0	180	23.6	0.23

TABLE 6 (Cont'd) - PHYSICAL AND CHEMICAL DATA

SEMET SOLVAY EFFLUENTS

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppm	Cyanide ppm
Coke Plant	11-8	Gray Medicinal Turbid	6.6	8.6	68	0	185	22.7	1.5
Primary and Secondary Indirect CGA Coolers	11-7	Colorless Faint coal gas Clear	5.4	7.7	100	4	150	-	-
Coke Quench	11-7	Black Faint coal gas Turbid	6.2	8.6	86	0	160	1.5	0.38
"	11-8	"	5.6	8.4	80	0	155	-	-
Light oil and wash oil decanter	11-7	Whitish, emulsified Strong coal gas Turbid	0.0	8.2	224	24	25	11.5	3.88
"	11-8	Grayish tan Strong coal gas and medicinal Turbid Some emulsified oil	0.0	8.1	206	20	40	8.8	116.0
No.1 Ammonia Still (Producing "B" liquor)	11-7	Dark brown Medicinal Clear	0.0	9.1	860	0	2350	742	2.6

TABLE 6 (Cont'd) - PHYSICAL AND CHEMICAL DATA

SEMET SOLVAY EFFLUENTS

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppm	Cyanide ppm
Coke Plant	11-8	Gray Medicinal Turbid	6.6	8.6	68	0	185	22.7	1.5
Primary and Secondary Indirect CGA Coolers	11-7	Colorless Faint coal gas Clear	5.4	7.7	100	4	150	-	-
Coke Quench	11-7	Black Faint coal gas Turbid	6.2	8.6	86	0	160	1.5	0.38
"	11-8	"	5.6	8.4	80	0	155	-	-
Light oil and wash oil decanter	11-7	Whitish, emulsified Strong coal gas Turbid	0.0	8.2	224	24	25	11.5	3.88
"	11-8	Grayish tan Strong coal gas and medicinal Turbid Some emulsified oil	0.0	8.1	206	20	40	8.8	116.0
No.1 Ammonia Still (Producing "B" liquor)	11-7	Dark brown Medicinal Clear	0.0	9.1	860	0	2350	742	2.6

TABLE 6 (Cont'd) - PHYSICAL AND CHEMICAL DATA

SEMET SOLVAY EFFLUENTS

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppm	Cyanide ppm
No.1 Ammonia Still (Producing "B" liquor)	11-8	Dark brown Medicinal Turbid	0.0	11.0	1460	0	4000	845	41.0
No.2 Ammonia Still (Producing crude liquor	11-7	Dark Brown Medicinal Clear	0.0	8.7	890	0	1560	900	2.4
"	11-8	Dark brown Medicinal and coal gas Turbid	0.0	11.9	1590	0	5300	790	5.0

pH, alkalinity, and hardness were quite high in the ammonia still effluents but in other effluents were not greatly different from intake waters. Phenols were by far the highest in ammonia still wastes and would be expected to contribute to the toxicity of these effluents. Cyanides were highest in the light oil and wash oil decanter waste and ammonia still wastes. The reason for the large difference in cyanides in the light oil and wash oil decanter waste and the No. 1 ammonia still waste on successive days is not known.

Toxicity to Fish

A summary of bio-assay results showing the comparative toxicity of the different effluent samples to fish is shown in Table 7. The data on which these results are based are shown in the Appendix at the end of this report. Twenty-four, 48, and 96 hour TL_m values and dilution volumes were computed as described in the section on bio-assay methods.

The results of the bio-assays on the samples taken on two successive days indicated most of the effluents were reasonably uniform in toxicity. The greatest variation was in the No. 2 ammonia still waste, which was considerably less toxic on the second day.

There were no major differences in 24, 48, and 96 hour TL_m values for any of the effluent samples indicating little or no accumulative effect on fish or else a loss of toxicity in a relatively short time period.

The samples of final combined (coke plant and oil gas generator) sewer effluent and coke plant effluent were toxic to fish. Little or no toxicity was apparent in the samples of oil gas generator plant effluent when adequate oxygen was maintained in the test concentrations. The combined effluent was somewhat less toxic on the second sample even though toxicity in the coke

TABLE 7 - SUMMARY OF BIOASSAY DATA

SEMET SOLVAY EFFLUENTS

Source	Date 1956	Effluent Flow mgd	TL_m (Median Tolerance Limit) (Per Cent Concentration 24 Hr.	48 Hr.	96 Hr.	Dilution Volume mgd
Combined Sewer	11-7		23	22	22	
	11-8		37	37	37	
	AVERAGE	13.0	30	29	29	31.9
Niagara River Intake	11-7		100% surv.	100% surv.	100% surv.	-
Oil Gas Generator Plant	11-7		100% surv.	100% surv.	100% surv.	-
	11-8		100% surv.	100% surv.	100% surv.	-
	AVERAGE	1.75	100% surv.	100% surv.	100% surv.	0.0
Oil Gas Holder Overflow	11-7		4.2	4.2	4.2	
	11-8		5.6	5.6	5.6	
	AVERAGE	Intermittent	4.9	4.9	4.9	-
Coke Plant	11-7		24	22	22	
	11-8		24	24	24	
	AVERAGE	11.25	24	23	23	37.7
Coke Quench	11-7		100% surv.	100% surv.	100% surv.	
	11-8	0.90	100	100	100	
	AVERAGE	0.90	100	100	100	-
Indirect Coolers	11-7	-	100% surv.	100% surv.	100% surv.	-

TABLE 7 (Cont'd) - SUMMARY OF BIOASSAY DATA

SOLVAY EFFLUENTS

Source	Date 1956	Effluent Flow mgd	TL_m (Median Tolerance Limit) (Per Cent Concentration) 24 Hr.	48 Hr.	96 Hr.	Dilution Volume mgd
No.1 Ammonia Still	11-7		1.20	0.90	0.90	
No.1 Ammonia Still	11-8		0.75	0.75	0.75	
AVERAGE		0.145	0.98	0.83	0.93	16.7
No. 2 Ammonia Still	11-7		0.80	0.80	0.80	
No. 2 Ammonia Still	11-8		2.40	2.10	2.10	
AVERAGE		0.129	1.45	1.45	1.45	8.8
Light Oil and Wash Oil Decanter	11-7		0.35	0.35	0.35	
	11-8		0.24	0.22	0.22	
AVERAGE			0.30	0.29	0.29	13.1

plant effluent remained the same. Indications are that there was a possible antagonistic action between the coke plant effluent and the oil gas generator plant, thus slightly reducing the toxicity in the combined waste. This difference may, however, be due to differences in sampling (the samples were hourly grabs composited over an 8 hour period).

Only one process effluent, the gas holder overflow that enters the oil gas generator plant was tested. While this sample was moderately toxic, the volume was evidently small enough so as to have no effect on the total oil gas generator effluent.

Among the process effluents from the coke plant, the light oil and wash oil decanter waste was the most toxic to fish as indicated by the lowest TL_m value. Wastes from both ammonia stills had a high degree of toxicity with the No. 1 still somewhat the most toxic.

Coke quench waters were only slightly toxic. In one sample there was no fish mortality during the test period but the fish were badly affected. In the other sample half of the fish succumbed.

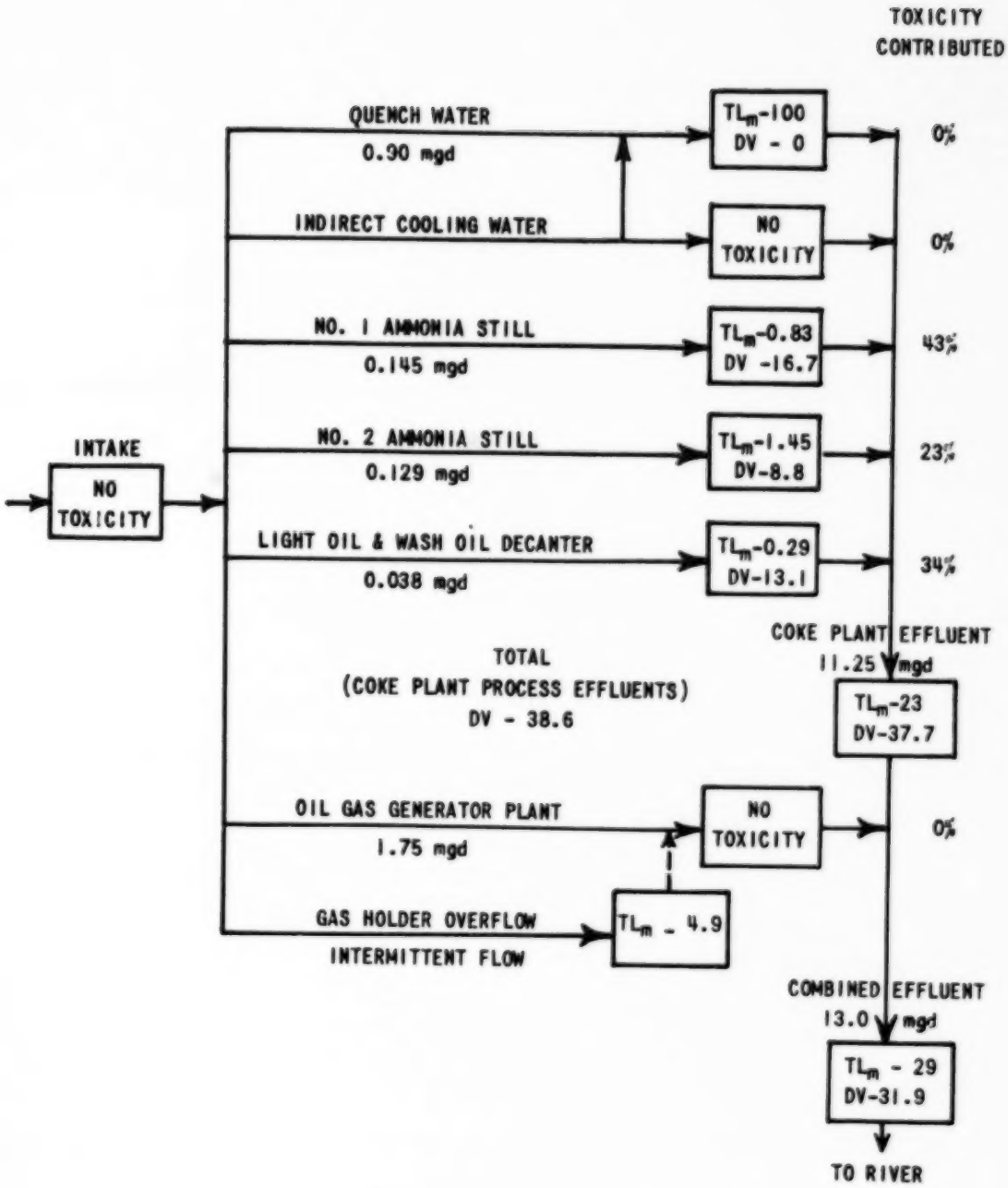
No toxicity was indicated in the indirect cooling waters which make up by far the largest volume of wastes from the coke plant.

Niagara River intake waters were not toxic.

Significance of Data

A schematic diagram showing the toxicity of process wastes and the percentage contribution of toxicity of each to the final effluent is shown in Figure 2.

The TL_m values are averages for the two samples taken. The dilution volumes were computed from the 96 hour TL_m and the effluent flow values given in Part I.



SCHEMATIC DIAGRAM SHOWING TOXICITY OF WASTES
DISCHARGED TO SEWER

SEMET SOLVAY DIVISION
ALLIED CHEMICAL AND DYE CORPORATION

FIGURE 2

As can be readily seen from this diagram practically all of the toxicity was contributed by the light and wash oil decanter waste and the ammonia still wastes.

Bio-assays conducted on some chemical compounds under similar experimental conditions to those of the effluents gave 96 hour TL_m values as follows:

Chemical	96 hour TL_m ppm
Phenol	40
O-cresol	24
Cyanide (CN)	0.24
Ammonia (N)	7.0
Sulfide (H_2S)	1.4
Benzene	56
Toluene	51
Xylene	28

The maximum values for these components in the effluents (Table 6) would indicate that phenol was not responsible for the toxicity in the combined sewer or coke plant effluents. Other phenolic compounds, however, have been reported toxic in concentrations as low as 0.2 p.p.m. Phenols would account for some of the toxicity in ammonia still wastes.

On the basis of the one sample analyzed cyanides could be responsible for the toxicity in the combined sewer effluent. The two coke plant samples, while of the same toxicity, varied considerably in cyanide content. In the second sample cyanide could account for most of the toxicity.

A similar situation prevailed in the light and wash oil decanter effluent. While cyanide was present to an extent in one sample which would more than account for the toxicity, the other sample, almost as toxic, had a much lower cyanide content. Phenols and cyanides together could apparently account for most of the toxicity in the ammonia still wastes. One sample, however, in which cyanide was extremely high, was not much more toxic than the others. The above differences appear to bear out the thought that toxicity cannot be directly determined from chemical information.

During this study, pH values of most of the effluent samples were at levels which would not be expected to have any adverse effect on aquatic life; generally, pH values below 5 and above 9 may have a direct lethal effect. Within these limits, however, a change in pH may have an effect by increasing or decreasing the toxicity of various chemicals to fish. The toxicity of metals, cyanides, and sulfides may be increased by a decrease in pH while the toxicity of ammonia is greater at higher pH values.

Dissolved oxygen values were at levels which would definitely affect aquatic life (Table 6) in some of the effluent samples. Oxygen depleting characteristics may have a definite effect on aquatic life unless adequate volumes of receiving water are available for dilution or assimilation. Low oxygen may also tend to increase the toxicity of certain chemicals (e.g. cyanide). For adequate protection of aquatic life, dissolved oxygen concentrations should be maintained at 5 p.p.m. or above in waters receiving toxic materials.

Oil may mix with other organic material, settle to the bottom in the form of a sludge, and have an adverse effect on bottom fish food organisms.

Small, sublethal quantities of oils, gasoline, phenols, and various

solvents, especially benzene derivatives, are known to impart a taste to fish flesh.

High water temperatures may have an effect in increasing the toxicity of some materials, reducing dissolved oxygen, and a direct effect on some organisms.

Color and turbidity apparently have no direct effect on fish. An indirect effect may be possible by a decrease in light penetration and consequently the productivity. Suspended materials may settle out and have an adverse effect on bottom food organisms and fish spawning.

CONCLUSIONS

While two days samples are not adequate for a complete picture of the variation in toxicity of effluents from a complex industry, the toxicity values on successive days were in fairly close agreement. The following conclusions are based entirely on the samples taken.

The combined sewer (oil gas generator and coke plant) effluent was toxic to fish. The dilution water estimated for safety to aquatic life (10 x dilution volume), approximately 450 cfs, is only a fraction of the flow in the Niagara River.

The oil gas generator plant effluent was non toxic but had a marked oxygen depleting effect.

The coke plant effluent was slightly more toxic than the combined effluent. Practically all of this toxicity was contributed by the light and wash oil decanter waste and the ammonia still wastes. The coke quench water was only slightly toxic and the indirect cooler water non toxic to fish.

In some of the samples phenols and cyanides could apparently account

for most of the toxicity. There was, however, much less difference in the toxicity of similar effluent samples than the wide variation in cyanides would indicate.

APPENDIX TABLE 1 -BIOASSAY DATA

Test Fish - Pethead Minnows
Dilution Water - Lake Erie

SHELL-SOLTAY DIVISION
ALLIED CHEMICAL AND DYE CORPORATION

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
												Effluent	22	0.2	7.8	80	4	195	Greyish-tan color. Slightly turbid. Oil and medicinal odor.
Combined Sewer	11-7-56	100	-																
6 hr.composite												Initial	22	5.0	8.2	90	2	165	
		56	5	10	2 hrs.	3 hrs.	6 hrs.	0	0	0	0	6 hrs.	22	3.4	7.5	-	-	-	
In Lab												Initial		6.2	8.2				Oxygen added (No oxygen D.O.-0.0)
5:30 PM 11/7		32	10	30	7 hrs.	7-22 hrs.	24-42 hrs.	10	0	0	0	42 hrs.		20.0	7.6				
Fish Added												Initial		6.6	8.2	94	0	160	
10:30 AM 11/8		18	5	10	30 hrs.	-	-	100	80	80	80	96 hrs.		4.4	7.6	94	4	150	
	Tlm (Median Tolerance Limit - Per Cent Concentration)							21	22	22	22								
													22	1.4	7.7	94	8	150	Greyish-tan color. Slightly turbid. Oil and medicinal odor.
Combined Sewer	11-8-56	100																	
6 hr.composite												Initial	Initial	-	-	-	-	-	
		56	4	4	1-20 hrs.	1-20 hrs.	1-20 hrs.	0	0	0	0	20 hrs.	20 hrs.	0.8	-	-	-	-	Low oxygen
In Lab												Initial	Initial	-	-	-	-	-	
5:00 PM 11/8		42	2	2	10 hrs.	10 hrs.	10-24 hrs.	0	0	0	0	24 hrs.	24 hrs.	0.4	7.3	-	-	-	Low oxygen
Fish Added												Initial	Initial	6.4	7.7	94	8	150	Oxygen added
1:30 PM 11/11		32	5	10	-	-	-	100	100	100	100	-	-	-	-	-	-	-	
													-	-	-	-	-	-	
		18	2	2	-	-	-	100	100	100	100								
	Tlm (Median Tolerance Limit - Per Cent Concentration)							37	37	37	37								
																			Oxygen added.
Oil-gas generator plant	11-7-56	100	5	10	-	-	-	100	100	100	100	Initial	Initial	0	7.2	82	12	190	Greyish-tan color. Slightly turbid. Strong medicinal and coal gas odor. Oxygen added.
												-		-	-	-	-	-	
6 hr.composite		Oxy 56	5	10	-	-	-	100	100	100	100	Initial	Initial	3.2	7.5	96	8	140	
In Lab												96 hrs.		18.6	7.3	-	-	-	
5:30 PM 11/7		56	5	10	4-18 hrs.	4-18 hrs.	27-44 hrs.	20	0	0	0	Initial	Initial	3.2	7.5	96	8	140	Low oxygen
Fish Added												44 hrs.	44 hrs.	0.8	7.4	-	-	-	
1:45 PM 11/8		32	5	10	-	-	-	100	100	100	100	Initial	Initial	4.8	7.8	86	2	135	
												96 hrs.		3.8	7.5	-	-	-	
																			No mortality when oxygen maintained.
	Tlm (Median Tolerance Limit - Per Cent Concentration)							100% surv	100% surv	100% surv	100% surv								
																			Oxygen added.
Oil-gas generator plant	11-8-56	100	2	2	-	-	-	100	100	100	100	Initial		0.2	7.4	8.8	10	190	Greyish-tan color. Slightly turbid. Strong medicinal and coal gas odor. Oxygen added
												-							
6 hr.composite		56	2	2	-	-	-	100	100	100	100								
In Lab																			
5:00 Pm 11/8		32	2	2	-	-	-	100	100	100	100								
Fish Added																			No mortality when oxygen maintained.
3:00 PM 11/10	Tlm (Median Tolerance Limit - Per Cent Concentration)							100% surv	100% surv	100% surv	100% surv								

APPENDIX TABLE 2 -BIOASSAY DATA

Test Fish - Fathead Minnows
Dilution Water - Lake Erie

SOLVAY PROCESS DIVISION
ALLIED CHEMICAL AND DYE CORPORATION

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Coke Plant	11-7-56	100	-									Effluent	22	4.6	8.2	92	0	180	Grayish-tan color. Slightly turbid. Strong medicinal odor. 3 fish dead, others barely alive in 7 hrs. (D.O.-6.4)
effluent																			
6 hr.composite		32	5	10	7 hrs.	7-22 hrs.	7-22 hrs.	0	0	0	0	Initial	22	6.8	8.2	94	0	185	
In Lab												22 hrs.	22	0.0	7.2	-	-	-	
5:30 PM 11/7		18	10	20	48 hrs.	-	-	100	80	80	80	Initial		7.0	8.2	94	0	150	(No oxygen-D.O.-4.6) Oxygen added.
Fish Added												96 hrs.		19.6	7.7	-	-	-	
10:45 AM 11/8		10	5	10	-	-	-	100	100	100	100	Initial		7.4	8.3	92	0	140	
												96 hrs.		4.6	7.7	-	-	-	
		TLm (Median Tolerance Limit - Per Cent Concentration)						24	22	22	22								
Coke Plant	11-8-56	100	-									Effluent	22	6.6	8.6	68	0	185	Gray color. Turbid. Medicinal odor. 4 dead in 7 hrs. (D.O.-6.4)
effluent																			
6 hr.composite		32	5	10	4 hrs.	5 hrs.	7-24 hrs.	0	0	0	0	Initial	22	7.4	8.4	88	0	175	
In Lab												24 hrs.	22	0.2	7.4				
5:00 PM 11/8		18	5	10	-	-	-	100	100	100	100	Initial		7.8	8.3	90	0	160	
Fish Added												96 hrs.		5.4	7.6				
11:00 AM 11/9		TLm (Median Tolerance Limit - Per Cent Concentration)						24	24	24	24								
Light Oil	11-7-56	100	-									Effluent	22	0.0	8.2	224	24	25	White, emulsified oil appearance. Turbid. Strong coal gas odor.
Decanter																			
6 hr.composite		3.2	2	2	15 min.	15 min.	15 min.	0	0	0	0	-	-	-	-	-	-	-	
In Lab																			
5:30 PM 11/7		1.0	5	10	2 hrs.	2 hrs.	2 hrs.	0	0	0	0	Initial	22	7.2	8.3	96	0	135	
Fish Added												2 hrs.	22	7.0	8.3				
2:00 PM 11/8		.56	5	10	4-18 hrs.	4-18 hrs.	4-18 hrs.	0	0	0	0	Initial		7.4	8.3	92	0	135	
												18 hrs.		6.2	8.1				
		.32	5	10	4-18 hrs.	-	-	60	60	60	60	Initial		7.4	8.3	90	0	135	
												90 hrs.		5.8	7.8				
		.18	5	10	-	-	-	100	100	100	100	Initial		7.0	8.3	90	0	140	
												96 hrs.		4.8	7.7				
		TLm (Median Tolerance Limit - Per Cent Concentration)						0.35	0.35	0.35	0.35								
Light Oil	11-8-56	100	-									Effluent	22	0.0	8.1	206	20	40	Grayish, tan color. Some emulsified oil. Turbid. Strong coal gas and medicinal odor.
Decanter																			
6 hr.composite		1.0	5	10	30 min.	1 hr.	1 hr.	0	0	0	0	Initial	22	6.8	8.2	94	0	135	
In Lab												1 hr.	22	6.6	8.2				
5:00 PM 11/8		.56	5	10	5 hrs.	6 hrs.	6-24 hrs.	0	0	0	0	Initial		7.0	8.2	90	0	135	
Fish Added												2 hrs.		6.4	8.0				
11:45 AM 11/9		.32	5	10	5 hrs.	6 hrs.	6-24 hrs.	0	0	0	0	Initial		7.4	8.2	90	0	135	
												24 hrs.		5.4	7.9				
		.18	5	10	28-46 hrs.	-	-	100	80	80	80	Initial		7.6	8.2	90	0	135	
												70 hrs.		4.0	7.6				
		TLm (Median Tolerance Limit - Per Cent Concentration)						0.24	0.22	0.22	0.22								

APPENDIX TABLE 3 -BIOASSAY DATA

SOLVAY DIVISION
ALLIED CHEMICAL & DYE CORPORATION

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
No.1 Ammonia	11-7-56	100	-	-								Effluent	22	0.0	9.1	860	0	2350	Dark brown color. Clear. Medicinal odor.
Still (Producing																			
"B" Liquor		3.2	2	2	15 min.	15 min.	15 min.	0	0	0	0	-		-	-	-	-	-	
8 hr.composite																			
In Lab		1.0	5	10	2-17 hrs.	26-43 hrs	-	60	40	40	40	Initial	22	7.6	8.5	98	0	185	
5:30 PM 11/7												96 hrs.	22	4.6	7.8	-	-	-	
Fish Added		.56	5	10	-	-	-	100	100	100	100	Initial		7.2	8.4	94	0	170	
3:30 PM 11/8												96 hrs.		4.2	7.7	-	-	-	
		.32	5	10	-	-	-	100	100	100	100	Initial		7.6	8.4	94	0	170	
												96 hrs.		-	-	-	-	-	
		Control	5	10	-	-	-	100	100	100	100	Initial		7.6	8.3	90	0	135	
														-	-	-	-	-	
		TLm (Median Tolerance Limit - Per Cent Concentration)						1.20	0.90	0.90	0.90								
No.1 Ammonia	11-8-56	100	-	-								Effluent	22	0.0	11.0	1460	0	4000	Dark brown color. Turbid. Medicinal odor.
Still (Producing																			
"B" Liquor		1.8	5	10	1 hr.	2 hrs.	2-18 hrs.	0	0	0	0	Initial	22	6.6	8.5	100	0	180	
8 hr.composite												18 hrs.	22	6.6	8.3	-	-	-	
In Lab		1.0	5	10	2-18 hrs.	2-18 hrs.	2-18 hrs.	0	0	0	0	Initial		6.8	8.6	100	0	175	
5:00 PM 11/8												18 hrs.		6.2	8.5	-	-	-	
Fish Added		.56	5	10	-	-	-	100	100	100	100	Initial		7.2	8.6	98	0	165	
4:00 PM 11/9												96 hrs.		4.0	7.7	-	-	-	
		TLm (Median Tolerance Limit - Per Cent Concentration)						0.75	0.75	0.75	0.75								
No.2 Ammonia	11-7-56	100	-	-								Effluent	22	0.0	8.7	890	0	1560	Dark brown color. Clear. Medicinal odor.
Still.																			
8 hr.composite		3.2	2	2	15 min.	15 min.	15 min.	0	0	0	0	-		-	-	-	-	-	
In Lab																			
5:30 PM 11/7		1.0	5	10	2-17 hrs	2-17 hrs.	-	20	20	20	20	Initial		7.2	8.4	98	0	165	
Fish Added												96 hrs.		4.2	7.6	-	-	-	
3:30 PM 11/8		.56	5	10	-	-	-	100	100	100	100	Initial		7.2	8.4	96	0	150	
												96 hrs.		3.2	7.6	-	-	-	
		.32	5	10	-	-	-	100	100	100	100	Initial		7.6	8.4	96	0	145	
												96 hrs.		-	-	-	-	-	
		TLm (Median Tolerance Limit - Per Cent Concentration)						0.80	0.80	0.80	0.80								

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APPENDIX **TABLE 4 -BIOASSAY DATA**

SEMET-SOLVAY DIVISION
ALLIED CHEMICAL & DYE CORPORATION

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	P H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
No.2 Ammonia Still	11-8-56	100	-	-								Effluent	22	0.0	11.9	1590	0	5300	Dark brown color.
8 hr.composite		3.2	2	2	3-19 hrs	3-19 hrs	3-19 hrs	0	0	0	0	-	22	-	-	-	-	-	Turbid.
In Lab												19 hrs.	22	0.0					Medicinal and coal gas odor.
5:00 PM 11/8		2.4	2	2	24 hrs	24-48 hrs	24-48 hrs	50	0	0	0	-		-	-	-	-	-	Low oxygen.
Fish Added																			
4:30 PM 11/9		1.8	5	10	-	-	-	100	100	100	100	Initial		6.6	8.4	96	0	165	
												96 hrs.		0.8	7.4	-	-	-	
		1.0	5	10	-	-	-	100	100	100	100	Initial		7.2	8.4	98	0	145	
												96 hrs.		1.2	7.4	-	-	-	
		.56	5	10	-	-	-	100	100	100	100	Initial		7.2	8.6	100	0	165	
												96 hrs.		2.2	7.6	-	-	-	
		Tlm (Median Tolerance Limit - Per Cent Concentration)						2.4	2.1	2.1	2.1								
Coke quench	11-7-56	100	5	10	-	-	-	100	100	100	100	Initial	22	6.2	8.6	86	0	160	Black color.
8 hr.composite																			Slightly turbid.
In Lab		56	5	10	-	-	-	100	100	100	100	96 hrs.	22	-	-	-	-	-	Faint coal gas odor.
5:30 PM 11/7												Initial		7.4	8.4	88	0	145	Fish effected but all survived.
Fish Added		32	2	2	-	-	-	100	100	100	100	96 hrs.		-	-	-	-	-	
5:00 PM 11/8												-		-	-	-	-	-	
		Tlm (Median Tolerance Limit - Per Cent Concentration)						100% surv	100% surv	100% surv	100% surv								
Coke quench	11-8-56	100	2	2	48 hrs.	48 hrs.	-	100	50	50	50	Initial	22	5.6	8.4	80	0	155	No fish mortality
8 hr.composite													22						Black color.
In Lab		56	2	2	-	-	-	100	100	100	100			-	-	-	-	-	Slightly turbid.
5:00 PM 11/8																			Faint coal gas odor.
Fish Added																			
4:00 PM 11/10																			
		Tlm (Median Tolerance Limit - Per Cent Concentration)						100	100	100	100								
Gas holder overflow	11-7-56	100	-	-								Effluent	22	0.0	6.5	120	124	70	Rusty brown color.
8 hr.composite		32	2	2	1-12 hrs	1-12 hrs	1-12 hrs	0	0	0	0	-		-	-	-	-	-	Very turbid.
In Lab																			Coal gas odor.
5:30 PM 11/7		10	2	2	1-12 hrs	1-12 hrs	1-12 hrs	0	0	0	0	-		-	-	-	-	-	
Fish Added																			
3:00 PM 11/8		5.6	2	2	24-48 hrs	24-48 hrs	24-48 hrs	100	0	0	0	-		-	-	-	-	-	
												48 hrs.		0.0	-	-	-	-	
		3.2	2	2	-	-	-	100	100	100	100	-		-	-	-	-	-	Low oxygen.
		Tlm (Median Tolerance Limit - Per Cent Concentration)						7.5	5.7	5.2	5.2								

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APPENDIX TABLE 5 -BIOASSAY DATA

SECRET-SULTAY DIVISION
ALLIED CHEMICAL AND DYE CORPORATION

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$)ppm	VERSENATE HARDNESS ppm.	
Gas holder	11-6-56	100	-	-								Effluent	22	0.0	-	-	-	-	Rusty brown color. Very turbid. Coal gas odor.
Overflow																			
6 hr.composite		10	2	2	2 hrs.	2 hrs.	2 hrs.	0	0	0	0	Initial		-	-	-	-	-	
In Lab												2 hrs.		1.6					
5:00 PM 11/8		5.6	2	2	23 hrs.	23 hrs.	-	50	50	50	50	-		-	-	-	-	-	
Fish Added																			
4:00 PM 11/10		3.7	2	2	-	-	-	100	100	100	100	-		-	-	-	-	-	
		TLm (Median Tolerance Limit)			- Per Cent Concentration)			5.6	5.6	5.6	5.6								
Primary, and	11-7-56	100	2	2	-	-	-	100	100	100	100	Effluent	22	5.4	7.7	100	4	150	Colorless. Clear. Very faint coal gas odor.
secondary, DGA																			
cooling coils		30	2	2	-	-	-	100	100	100	100								
6 hr.composite																			
In Lab		TLm (Median Tolerance Limit			- Per Cent Concentration)			100% surv	100% surv	100% surv	100% surv								No fish mortality.
5:30 PM 11/7									No toxicity										
Fish Added																			
9:30 AM 11/8																			
Niagara River	11-7-56	100	2	2	-	-	-	100	100	100	100	Initial	22	-	-	-	-	-	Colorless
Intake												96 hrs.		4.4	7.6	90	4	145	Clear No odor
In Lab																			
5:30 PM 11/7		TLm (Median Tolerance Limit			- Per Cent concentration)			100% surv	100% surv	100% surv	100% surv								No fish mortality.
Fish Added									No toxicity										
7:30 PM 11/7																			

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